Synthese en reacties van dehydroadamtaan

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SUMMARY

This thesis deals with the synthesis of dehydroadamantane (tetracyclo[4, 3, 1, $0^{2,4}$, $0^{3,8}$] decane) (10) and of 2-mono- and 2, 4-disubstituted adamantanes (II and III).

In chapter 1 a brief survey of the known methods for the preparation of adamantane and its derivatives is given.

The synthesis of dehydroadamantane (10) by an intramolecular insertion reaction of carbena adamantane (I) is the subject of chapter 2. The requisite carbene was generated by pyrolysis of the lithiumsalt of the tosylhydrazone of adamantanone (17) (Bamford-Stevens reaction). An alternative synthesis involving oxidation of the hydrazone of adamantanone (13) with activated manganese dioxide did not lead to the desired dehydroadamantane (10) but rather to adamantylidene azine (14).

Chapter 3 is concerned with ring opening reactions of the cyclopropane ring of dehydroadamantane (10) induced by a variety of electrophilic reagents resulting in 2-mono- and 2, 4-disubstituted adamantanes (II and III).

Some of these reactions are novel for cyclopropanes, e.g. the additions of iodochloride, iodobromide and nitrosylchloride and the coupled additions of halogen cations and nucleophilic reagents. These coupled additions proceed in a stereospecific way. The ring opening products of dehydroadamantane served as starting materials for the syntheses of other secondary substituted adamantanes. Dehydroadamantane did not enter into cycloadditions with benzyne, dicyanoacetylene and dicarbomethoxyacetylene.

On reduction of 2e, 4e- and 2a, 4e- diiodoadamantane ((33) and (34)) with lithium aluminium hydride dehydroadamantane was formed as the major product along with adamantane. This ring closure reaction thus constitutes a second approach to the synthesis of dehydroadamantane.

The elucidation of the stereochemistry of the 2, 4-disubstituted adamantanes, described in this thesis, by means of PMR spectroscopy is the subject of chapter 4.

In chapter 5 the ring opening reaction of the β-bromoketone 4e-bromoadamantanone (61) by silverperchlorate in a mixture

of water and acetone, resulting in the formation of bicyclo [3, 3, 1] nonene-2-carboxylicacid-7 (75), is explained by a mechanism analogous to that of the quasi- Favorsky reaction of α-bromoketones. The ring closure reactions of two bicyclo [3, 3, 1] nonane derivatives in acid medium furnish mixtures of adamantane (1), 2-hydroxyadamantane (22), di(adamantyl-2) ether (81) and 2-oxa-tricylo $[4, 3, 1, 1^{4,8}]$ -undecane (80).